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POTASSIUM ZIRCONIUM REACTIONS

DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

BY

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1928

Published 1930

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TABLE OF CONTENTS

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	PAGES
Zirconium Sulfate as a Reagent for the Detection of Potassium. 50 1515 (1928)	1515-1522
Zirconium II. Detection of Potassium by Zirconium Sulfate in the Presence of Ammonium Ions. 50, 2985 (1928)	2985-2987
Zirconium III. Influence of Lithium, Rubidium, Cesium, and Magnesium upon the Detection of Potassium of Zirconium Sulfate. 51, 1062 (1929)	1062-1065
Zirconium IV. Removal of Zirconium by Phosphates. 51, 1311 (1929)	1311-1313
Zirconium V. Detection of Traces of Potassium in the Presence of Zirconium. 51, 3238 (1929)	3238-3241

Reprint from the Journal of the American Chemical Society, 50, 1515 (1928).]

[Contribution from the Chemical Engineering Department, The Ohio State University]

ZIRCONIUM SULFATE AS A REAGENT FOR THE DETECTION OF POTASSIUM[1]

By Rufus D. Reed and James R. Withrow

Received July 27, 1927 Published June 5, 1928

Work under way in this Laboratory indicated the possibility of using zirconium sulfate as an alternative test for the detection of potassium. Potassium sulfate has long been known as a reagent for the precipitation of zirconium.[2] No one appears to have taken the trouble to find how sensitive zirconium sulfate itself would be in the detection of potassium. Therefore the sensitiveness of a zirconium sulfate solution for potassium was investigated.

Experimental

To investigate the sensitiveness of zirconium sulfate solution as a qualitative test for potassium it was necessary to prepare the following reagents and to determine their purity.

Zirconium Sulfate Solution.—This solution was prepared by stirring powdered zirconium sulfate with distilled water for four hours. The solution was allowed to stand overnight at room temperature. It was filtered and analyzed to determine purity to preclude interfering substances. It contained no cerium earth metals, cobalt or tartrate. Quantitative analysis for zirconium by the Lundell and Knowles method[3] showed 0.2096 g. of zirconium sulfate per cc. of solution. This solution was prepared at 28°. It would deposit crystals on standing overnight but these could be dissolved by warming the bottle of solution in hot water for a few minutes.

Potassium Sulfate Solution.—A saturated potassium sulfate solution containing 0.0545 g. of elemental potassium per cc. was prepared. To preclude possible interfering substances, this solution was analyzed qualitatively and found free from hydroxyl, carbonate, sulfide, thiosulfate, phosphate, sodium and ammonium ions. Dilution of portions of this stock solution gave the more dilute solutions used.

Sodium Sulfate Solution.—To determine the effect of the sodium ion on the detection of potassium by zirconium sulfate, a saturated solution of potassium free sodium

[1] Read before Detroit meeting, September, 1927.

[2] Fresenius, "Qualitative Chemical Analysis," C. A. Mitchell's translation of 17th edition, John Wiley and Sons, Inc., New York, 1921, p. 182; Venable, "Zirconium and Its Compounds," Chemical Catalog Co., New York, 1922, pp. 81–84.

[3] Lundell and Knowles, This Journal, 41, 1801 (1919).

sulfate was prepared. Mixing of this solution with the potassium sulfate solution gave the mixtures of sodium and potassium sulfates used.

Sodium Cobaltic Nitrite Solution.—For comparison of sensitiveness of sodium cobaltic nitrite and zirconium sulfate for the detection of potassium, a solution of sodium cobaltic nitrite was prepared according to the method of Scott.[4]

General Procedure for Potassium Detection.—In all the series of experiments in which potassium was tested for by zirconium sulfate, exactly 1cc. portions of potassium sulfate solutions of varying concentrations were pipetted into dry test-tubes. Exactly 1cc. portions of zirconium sulfate solution were added. The mixtures after shaking were allowed to stand at room temperature for one hour. Then the tubes were immersed in ice water until a reaction was noticed. At the start of the run, the walls of the tubes were well rubbed with a glass rod to promote

TABLE I

SENSITIVENESS OF ZIRCONIUM SULFATE SOLUTION AS A TEST FOR POTASSIUM

Total volume, 2 cc. Zirconium sulfate, 0.2096 g. per test

Expt.	K, g. per sample	Results at room temperature	Results on cooling to 0°C.
1	0.05455	Precipitate at once	...
2	.02728	Precipitate at once	...
3	.01818	Cloudy at once	...
4	.01362	Precipitate in one-half hour Precipitate in one-half hour	...
5	.00909	Slight precipitate in one-half hour	...
6	.00495	Cloudy in one hour	More cloudy in one-half hour, precipitate in one hour
7	.00260	None one hour	Cloudy in one-half hour, precipitate in one hour
8	.00176	None one hour	Cloudy in one hour, precipitate in one and one-half hours
9	.00107	None one hour	Cloudy one and one-half hours, precipitate in 2 hours
10	.00072	None one hour	Slightly cloudy in one and one-half hours, more so in two hours, precipitate in 2 and one-half hours
11	.00053	None one hour	Slightly cloudy in one and one-half hours, more so in 2 hours, precipitate in two and one-half hours
12	.00030	None one hour	Slight precipitate in one hour
13	.00007	None one hour	Slightly cloudy in two hours
14	.00000	None one hour	Slightly cloudy in two hours, precipitate in two and one-half hours
15	.00000	None one hour	Clear in two and one-half hours
16	.00000	None one hour	Slight precipitate in four hours

[4] Scott, "Qualitative Chemical Analysis," 4th edition, 2d printing, D. Van Nostrand Co., New York City, 1923, p. 330.

crystallization. This rubbing was repeated at half-hour intervals throughout the run.

Sensitiveness of Zirconium Sulfate Solution as a Test for Potassium.—To determine the sensitiveness of zirconium sulfate for potassium when no possible interfering ions were present, a series of experiments was made, varying the amount of potassium and keeping all other factors constant. The results are given in Table I.

Discussion.—On cooling in ice water the deposit formed in Expt. 11 containing 0.00053 g. of potassium (0.0068 molal potassium sulfate or 0.05% elemental potassium) was slightly more than in Expt. 14 containing no potassium. The deposit in Expt. 12 containing 0.3 mg. of potassium although formed after one hour's cooling did not increase in magnitude on standing. This deposit and the deposit in Expt. 13 containing 0.07 mg. of potassium were of about the same magnitude as the deposit in the blank Expt. 14. The formation of deposits in the two blanks, Expts. 14 and 16, emphasized the need of running concurrently a blank in tests for traces of potassium with zirconium sulfate.

The appearance of the precipitate varied. If it came at once on adding the reagent or after rubbing the walls of the tube with a stirring rod, it appeared to be amorphous. If it formed slowly with no agitation, it was needle shaped and collected in fan-like bundles.

An idea of the amount of potassium present in a solution could be gained from the time required for the appearance of a deposit. If 18.2 mg. of potassium was present in 2 cc. of mixture, a deposit or cloudiness was formed at once. Those solutions containing less than 18.2 mg. of potassium and more than 4.95 mg. of potassium gave a precipitate or cloudiness within an hour at room temperature. Those solutions containing 0.5 mg. to 2.6 mg. of potassium per cubic centimeter gave a precipitate only after cooling in ice water for from one to two and one-half hours depending upon the amount of potassium present.

Comparison of Sensitiveness of Zirconium Sulfate Solution for Potassium with that of Sodium Cobaltic Nitrite Test for Potassium.—To compare the sensitiveness of these two reagents, a series of tests for potassium with sodium cobaltic nitrite was made. The method of testing with sodium cobaltic nitrite was that of Scott.[5] A comparison with a blank was made where there was any doubt as to turbidity or deposit. The results appear in Table II.

Discussion.—Consideration of the time factor showed that: (1) both sodium cobaltic nitrite and zirconium sulfate gave immediate tests for potassium when 18.18 mg. of potassium was present. (2) With lower concentrations of potassium, the sodium cobaltic nitrite solution is a quicker test for potassium than zirconium sulfate solution. The presence

[5] Ref. 4, p. 151.

TABLE II

COMPARISON OF SENSITIVENESS OF SODIUM COBALTIC NITRITE TEST AND OF ZIRCONIUM SULFATE TEST FOR POTASSIUM

Total volume, 2 cc.

Expt.	K, g. per sample	Time for reaction with sodium cobaltic nitrite	Time for reaction with zirconium sulfate. Cooling to 0°C.
1	0.01818	Immediate precipitate	Immediate cloudiness at room temperature. No cooling
2	.00107	Slight precipitate in five minutes	Cloudy in one and one-half hours, cooling; precipitate in two hours, cooling
3	.00072	Slight precipitate in five minutes	Cloudy in two hours, cooling; precipitate in two and one-half hours
4	.00053	Slightly turbid in five minutes, slight precipitate in ten minutes	Precipitate in two hours, cooling
5	.00030	Slightly turbid in fifteen minutes, slight precipitate in one hour	Slight precipitate in one hour, no increase on standing. Same bulk of precipitate as blank at end
6	.00014	Slightly turbid in one hour, slight precipitate in two and one-half hours	No more test than blank
7	.00010	Very slight precipitate in five hours	No experiment run
8	.00007	Slight precipitate in twenty-three hours	No more test than blank
9	.00005	Clear, twenty-three hours	No experiment run
10	.00000	Clear, twenty-three hours	Slightly cloudy in two hours, precipitate in two and one-half hours

of 0.53 mg. to 0.3 mg. of potassium can be detected with sodium cobaltic nitrite within five to fifteen minutes, while it required one hour at room temperature and two hours' cooling to 0° to detect 0.5 mg. of potassium with zirconium sulfate solution.

As the sodium cobaltic nitrite test is usually applied according to directions of Scott[5] the absence of a precipitate with sodium cobaltic nitrite after ten to twenty minutes is considered as satisfactory proof of the absence of potassium. This work showed that as ordinarily applied the sodium cobaltic nitrite test is a little more delicate for potassium than zirconium sulfate when used for the longer time which we find desirable. Allowing the sodium cobaltic nitrite test, however, to stand for a longer time than is customary and comparing to a blank test, the sensitiveness of sodium cobaltic nitrite for potassium is 0.07 mg. of potassium as compared to 0.53 mg. of potassium with zirconium sulfate solution.[6]

[6] Bray, THIS JOURNAL, **31**, 611 (1909), obtained with the sodium cobaltic nitrite test a turbidity within one to four minutes with 0.3 mg. of potassium, while we did not secure therewith a slight turbidity until fifteen minutes and a slight precipitate in one

Effect of Sodium Ion on the Detection of Potassium by Zirconium Sulfate Solution.—In qualitative analysis potassium ions are generally associated with sodium ions, ammonium ions and various anions. While the ammonium ions and interfering anions can be removed by evaporation with hydrochloric or sulfuric acid and gentle ignition, the sodium ion remains. Therefore it is necessary to determine the extent to which the sodium ion interferes with the detection of potassium by zirconium sulfate solution. The results of this work are given in Table III.

TABLE III

THE EFFECT OF SODIUM ION UPON THE DETECTION OF POTASSIUM BY ZIRCONIUM SULFATE SOLUTION

Total volume, 2 cc. Zirconium sulfate per test, 0.2096 g.

Expt.	K, g. per sample	Na, g. per sample	Na/K	Results at room temperature	Results on cooling to 0°C.
1	0.03632	0.0266	0.7324	Precipitate at once	...
2	.02728	.0399	1.4646	Precipitate, few minutes	...
3	.01816	.0532	2.929	Precipitate, one hour	Increased
4	.01362	.0598	4.394	Precipitate, one hour	Increased
5	.00909	.0665	7.317	None, one hour	Precipitate, one-half hour
6	.00495	.0725	14.65	None, one hour	Precipitate, one hour
7	.00304	.0748	24.58	None, one hour	Precipitate, one hour
8	.00260	.0760	29.26	None, one hour	Precipitate, one hour
9	.00210	.0767	36.19	None, one hour	Small precipitate, one hour
10	.00000	.07441	.....	None, one hour	Opalescence, four hours
11	.00000	.0000	.....	None, one hour	Precipitate, four hours
12	.00176	.07201	41.9	None, one hour	Precipitate, one hour
13	.00107	.07295	68.0	None, one hour	Precipitate, two and one-half hours
14	.00072	.07343	102.4	None, one hour	Precipitate, two and one-half hours
15	.00053	.07368	139.0	None, one hour	Precipitate, one and one-half hours
16	.00030	.07401	246.7	None, one hour	Precipitate, one and one-half hours
17	.00007	.07432	1061.0	None, one hour	None, two and one-half hours
18	.00000	.07441	.....	None, one hour	Cloudy, one and one-half hours; precipitate, two hours

Discussion.—This work indicated that in the presence of very concentrated sodium sulfate solution, zirconium sulfate solution would detect

hour; but our results showed that by allowing the sodium cobaltic nitrite test to stand for one day, a test for 0.07 mg. of potassium would be secured while Bray did not push his test farther than 0.1 mg. of potassium, for which he obtained a precipitate in six to ten hours. We secured a test for this amount of potassium in five hours. Bray used a total volume of 10 cc., while we used a total volume of 2 cc., obtaining more sensitive results.

1.76 mg. of potassium in 2 cc. of mixture. Expt. 18, a blank, indicated that cooling for so long a time as two hours might cause a deposit to form when no potassium had been added, thus prohibiting prolonged cooling.

Comparison of the work in Table III with that in Table I indicated that: (1) the presence of sodium sulfate lowered the sensitiveness of zirconium sulfate for potassium from 0.53 mg. to 1.76 mg. (2) When potassium was present to the extent of 9 mg. or more, the presence of sodium retarded the test for potassium with zirconium sulfate about half an hour—it doubled the time. When potassium was present in amounts less than 9 mg. and 1.76 mg. or more, there was little or no difference in the time required for detection of potassium with zirconium sulfate. For amounts of potassium below 1.76 mg., the presence of sodium did not affect the time required for detection of potassium, but caused a deposit to form when no potassium had been added. As in the corresponding Experiment 12, Table I, in which no sodium was present, Expt. 16 containing 0.3 mg. of potassium gave a deposit with zirconium sulfate sooner than some of the more concentrated solutions of potassium. The amount of the deposit was of the same magnitude as that of the blank, indicating the need of a blank for comparison at low potassium concentrations.

Influence of Concentration of Zirconium Sulfate Solution on Detection of Potassium Both in the Presence and Absence of Sodium.—The stock solution was diluted to one-half strength in an attempt to eliminate precipitation in the blank. A dilute solution of the reagent would not crys-

TABLE IV

INFLUENCE OF CONCENTRATION OF ZIRCONIUM SULFATE SOLUTION UPON TEST FOR POTASSIUM BOTH IN THE PRESENCE AND ABSENCE OF SODIUM

Total volume, 2 cc. Zirconium sulfate, 0.1048 g.

Expt.	K, g. per sample	Na, g. per sample	Na/K	Results in one hour, room temp.	Results on cooling to 0°C.
1	0.00000	....	..	Opalescence	No change, four and one-half hours
2	...	0.07441	...	Opalescence	No change, four and one-half hours
3	...	.03720	...	Opalescence	No change, four and one-half hours
4	.0026	.07485	29.26	Cloudy	Small precipitate, one hour
5	.0026	....	...	None	Small precipitate, one hour
6	.00176	.07201	41.9	None	Opalescent, one hour; precipitate, one and one-half hours
7	.00176	....	...	None	Opalescent, one and one-half hours; precipitate, two hours
8	.00072	.07343	102.4	Opalescent	Cloudy, two and one-half hours; precipitate, four and one-half hours
9	.00072	....	...	Opalescent	Increased, three hours; no precipitate, four and one-half hours
10	.0003	....	...	None	Opalescent, one hour; no change, four and one-half hours
11	.0003	.07401	246.7	None	Opalescent, one hour; no change, four and one-half hours

tallize out on standing and so the warming up, mentioned in the section on preparation of zirconium sulfate, would be avoided. The results appear in Table IV.

Discussion.—In all experiments containing sodium sulfate except the blank 3, a deposit of apparently hydrated sodium sulfate formed on cooling to 0°. This would be dissolved on warming to room temperature for a few minutes. Any potassium zirconyl sulfate which might be present was undissolved.

The degrees of opalescence in the blanks 1, 2, 3 and in 10 and 11 containing 0.3 mg. of potassium were the same. This indicated that 0.3 mg. of potassium could not be detected by 10.48% zirconium sulfate. Expt. 9, containing 0.72 mg. of potassium, gave more opalescence after three hours' cooling than the blanks.

Comparing the results given above with the corresponding results in Table I and III where the concentrated zirconium sulfate was used showed: (1) in the absence of sodium, 20.96% zirconium sulfate solution detected 0.5 mg. of potassium while 10.48% zirconium sulfate solution detected 0.7 mg. of potassium. Either solution failed to detect the presence of 0.3 mg. of potassium in 2 cc. of mixture. Dilution of the reagent did not lower the sensitiveness of zirconium sulfate for potassium, but in the presence of sodium the dilution of the zirconium sulfate increased its sensitivity for potassium from 1.76 mg. to 0.7 mg. This increase in sensitivity was due to the non-formation of a deposit in the blank which occurred when the concentrated zirconium sulfate was used. (2) In the absence of sodium, the time required for the detection of potassium by zirconium sulfate was increased about one-half hour in all experiments. In the presence of sodium, the dilution of reagent increased the time required to detect potassium half an hour in the case of 1.76 mg. of potassium only.

The absence of a misleading deposit in the blank removed the serious objection that it was not a sure test for small amounts of potassium and increased the sensitivity of the test when sodium was present.

Summary of Conclusions

1. A concentrated zirconium sulfate solution detected 0.00053 g. of potassium (0.0068 molal potassium sulfate, 0.05% elemental potassium or 0.5 mg. of potassium) or more, when no sodium was present. It detected 1.76 mg. of potassium when sodium was present.

2. Large amounts of sodium sulfate retarded the detection of potassium in concentrated solutions but had little or no effect when the amount of potassium was small.

3. Zirconium sulfate when applied for the longer time we found necessary is almost as delicate a test for potassium as is sodium cobaltic nitrite when the latter is applied in the usual way. If the latter test is allowed to

run for a longer time than is customary, it can be made more sensitive for potassium than zirconium sulfate solution.

4. With dilute solutions of potassium sulfate—0.5 mg. of potassium—a comparison blank test with water and zirconium sulfate was needed. When sodium was present, a blank using sodium sulfate and zirconium sulfate was used for comparison with the solution tested.

5. Dilution of the zirconium sulfate solution to 10.48%, or one-half strength, had little or no effect upon its sensitiveness for potassium in the absence of sodium and increased the sensitiveness for potassium from 1.76 mg. of potassium to 0.7 mg. of potassium in the presence of sodium. No deposit in the blank test was formed.

6. To detect potassium with zirconium sulfate, add to the solution to be tested an equal volume of zirconium sulfate solution. If a deposit does not form at room temperature, cool in ice water. With small amounts of potassium a comparison with a blank is necessary.

COLUMBUS, OHIO

[Reprint from the Journal of the American Chemical Society, 50, 2985 (1928).]

[Contribution from the Chemical Engineering Department, The Ohio State University]

ZIRCONIUM. II. DETECTION OF POTASSIUM BY ZIRCONIUM SULFATE IN THE PRESENCE OF AMMONIUM IONS[1]

By Rufus D. Reed and James R. Withrow

Received August 6, 1928 Published November 6, 1928

We have shown that zirconium sulfate can be used to detect potassium and that the test can be applied in the presence of sodium.[2] Ammonium ions must be eliminated prior to testing for potassium with other reagents such as sodium cobaltic nitrite, chloroplatinic acid or perchloric acid. The sensitivity of zirconium sulfate for potassium in the presence of ammonium ions was therefore investigated.

The results indicated that zirconium sulfate solution will detect 0.48 mg. of potassium in 2 cc. of reaction mixture in the presence of large amounts of ammonium sulfate. This was practically the same sensitiveness of this reagent for potassium in the absence of ammonium as in the previous work.

[1] In memory of Ira Remsen.

[2] Reed and Withrow, This Journal, 50, 1515 (1928).

Concerning the action of alkali sulfates on zirconium sulfate, Fresenius[3] stated: "A concentrated solution of potassium sulfate rapidly produces a white precipitate of potassium zirconium sulfate. . . . Sodium sulfate and ammonium sulfate do not produce a precipitate." No reference was found indicating the effect of the presence of ammonium sulfate on the reaction between zirconium sulfate and potassium sulfate.

Experimental

In order to determine the sensitiveness of zirconium sulfate for potassium in the presence of ammonium it was necessary to prepare the following solutions.

Zirconium Sulfate Solution.—Impure zirconium sulfate was dissolved in water and the zirconium precipitated by a slight excess of sodium hydroxide. The hydroxide was washed by decantation and filtered and washed until 10 cc. of the filtrate evaporated to dryness and taken up with 2 cc. of water gave no test with sodium cobaltic nitrite. The moist zirconium hydroxide was dissolved in concentrated sulfuric acid. The somewhat dilute solution was concentrated overnight at 60° and allowed to stand for several days to reach constant composition. This solution was found to contain 0.1131 g. of zirconium sulfate and 0.0363 g. more sulfate per cc. due to excess sulfuric acid.

Potassium Sulfate Solution.—This was prepared from C. P. salt and water. Its strength was determined by evaporating a portion to dryness and igniting.

Ammonium Sulfate Solution.—The C. P. salt was dissolved in water. The solution was analyzed for ammonium by the distillation method.[4]

The solutions tested for potassium were prepared by mixing known amounts of the potassium and ammonium sulfate solutions.

Procedure

The procedure was exactly the same as given under the general procedure in the work previously published.[5] The results appear in the table.

TABLE I

SENSITIVENESS OF ZIRCONIUM SULFATE FOR POTASSIUM IN THE PRESENCE OF AMMONIUM IONS

Total volume 2 cc. $Zr(SO_4)_2$, 0.1131 g. per test

Expt.	K, g. per sample	NH_4, g. per sample	Results (time for appearance of a precipitate)
1	0.0000	0.05985	Clear and no ppt. in 5.5 hours at 0°
2	.0000	.01197	Clear and no ppt. in 5.5 hours at 0°
3	.0000	.00599	Clear and no ppt. in 3.5 hours at 0°. Tube broke
4	.02378	.02990	Ppt. in 10 min. at room temperature
5	.0158	.03990	Cloudy in 1 hour at room temp.; ppt. in 10 min. at 0°
6	.0048	.0539	Ppt. in 1 hour at 0°
7	.0024	.0569	Cloudy in 1 hour; ppt. in 1.5 hours at 0°
8	.00095	.0586	Cloudy in 1.5 hours; ppt. in 2 hours at 0°
9	.00058	.0591	Very slight ppt. in 2 hours; increased in 2.5 hours at 0°
10	.00048	.0593	Very slight ppt. in 2.5 hours; increased in 5.5 hours at 0°

[3] Fresenius, "Qualitative Chemical Analysis," C. A. Mitchell's translation of 17th edition, John Wiley and Sons, New York, **1921**, p. 182.

[4] Treadwell and Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, 6th ed., **1924**, pp. 72–73.

[5] Ref. 1, p. 1516.

Discussion

The deposits in Expts. 9 and 10 containing 0.58 mg. and 0.48 mg. of potassium were very small but could be detected by comparison with a blank.

The results indicated that zirconium sulfate will detect 0.48 mg. or more of potassium in 2 cc. of reaction mixture in the presence of large amounts of ammonium ions. This is a distinct advantage over other tests, in all of which ammonium interferes. Bray[6] found "With 1 mg. of NH_4 a precipitate formed in about 10 minutes (with sodium cobaltic nitrite); with 0.5 mg. on standing several hours." Ammonium salts also give precipitates with tartaric acid, perchloric acid and chloroplatinic acid. With perchloric acid or chloroplatinic acid the amount of potassium must be large or alcohol must be added. Zirconium sulfate will detect potassium when present to the extent mentioned in the presence or absence of ammonium ions and no alcohol is needed.

Summary

The sensitiveness of zirconium sulfate for potassium in the presence of ammonium ions was found to be 0.48 mg. or more of potassium per 2 cc. of reaction mixture. This is practically the same sensitiveness of zirconium sulfate for potassium when no other metal ions were present. This detection in the presence of ammonium is a distinct advantage over the other tests for potassium.

COLUMBUS, OHIO

[6] Bray, THIS JOURNAL, **31**, 633 (1909).

[Reprint from the Journal of the American Chemical Society, 51, 1062 (1929).]

[Contribution from the Chemical Engineering Department, The Ohio State University]

ZIRCONIUM. III. INFLUENCE OF LITHIUM, RUBIDIUM, CESIUM AND MAGNESIUM UPON THE DETECTION OF POTASSIUM BY ZIRCONIUM SULFATE[1]

By Rufus D. Reed and James R. Withrow

Received October 20, 1928 Published April 5, 1929

We have shown the availability of zirconium sulfate as a reagent for potassium in the presence of sodium[2] and ammonium.[3] The less frequently occurring members of the fifth group, rubidium and cesium, both interfere with the detection of potassium by sodium cobaltic nitrite, perchloric acid or chloroplatinic acid. Lithium can be separated from ions of these elements by perchloric acid or chloroplatinic acid. Tread-

[1] The authors are indebted to the Chemical Department of this University in that Professor Marion Hollingsworth of the Analytical Chemical Division of that Department furnished the rubidium and cesium chlorides used as the basis of part of this work.

[2] Reed and Withrow, This Journal, 50, 1519 (1928).

[3] Reed and Withrow, *ibid.*, 50, 2985 (1928).

well-Hall states concerning sodium cobaltic nitrite and lithium,[4] "moderate amounts of alkaline earth elements or of lithium and sodium do not interfere." Concerning magnesium Prescott and Johnson[5] stated, "potassium and large amounts of sodium may be readily detected in the presence of magnesium." Yet because of interference with the detection of small amounts of sodium, magnesium is removed prior to testing for the fifth group, to determine whether these fifth group elements would interfere with the detection of potassium by zirconium sulfate. The sensitiveness of this reagent for potassium in the presence of lithium, rubidium, cesium and magnesium was therefore investigated.

The results indicated that in a 2-cc mixture, zirconium sulfate detected 1.0 mg. or more potassium in the presence of 50 mg. of lithium sulfate, 16.6 mg. of rubidium sulfate or 11.6 mg. of cesium sulfate. It also detected 0.5 mg. or more of potassium in the presence of 50 mg. of magnesium sulfate. With no possibly interfering ions present, the zirconium sulfate reagent detected 0.5 mg. or more potassium.

The literature indicated that while Rosenheim and Frank[6] had prepared, "by the use of rubidium and cesium sulfates, compounds analogous in external appearance and in composition" to potassium zirconyl sulfate, no one had ascertained whether the presence of lithium, rubidium, cesium or magnesium would interfere with the reaction between potassium sulfate and zirconium sulfate, though the reference indicated the probability that they would interfere.

Experimental

In order to determine the effect of lithium, rubidium, cesium and magnesium upon the detection of potassium by zirconium sulfate, the following solutions were prepared.

Potassium Sulfate Solution and Zirconium Sulfate Solution.—These solutions were prepared in exactly the same way as described in the work on effect of ammonium ion on detection of potassium by zirconium sulfate.[2] The zirconium sulfate solution analyzed for 0.0871 g. of zirconium sulfate and an excess of 0.0395 g. of sulfate ion, due to excess sulfuric acid, per cubic centimeter.

Lithium Sulfate, Rubidium Sulfate, Cesium Sulfate and Magnesium Sulfate Solutions.—These solutions were prepared by dissolving potassium-free anhydrous salts in water and diluting to known volume.

Procedure.—Solutions containing known amounts of potassium and of either lithium, rubidium, cesium or magnesium sulfate were prepared by mixing known volumes of the proper solutions. The procedure of the test was the same as given in the preceding work.[2] The results appear in the table.

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[4] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, New York, 1920, Vol. I, p. 85.

[5] Prescott and Johnson, "Qualitative Chemical Analysis," revised by J. C. Olsen, D. Van Nostrand Co., New York, 1918, p. 242.

[6] Rosenheim and Frank, *Ber.*, 38, 812–817 (1905).

TABLE I

SENSITIVITY OF ZIRCONIUM SULFATE FOR POTASSIUM IN THE PRESENCE OF LITHIUM, RUBIDIUM, CESIUM AND MAGNESIUM

Total volume 2 cc. $Zr(SO_4)_2$ per test, 0.0871 g.

Expt.	K, g.	Sulfate	G.	Results and time for precipitation
1	0.0000	Li_2SO_4	0.0550	Cloudy, 3.5 hours; same in 5 hours at 0°
2	.0010	Li_2SO_4	.0500	Sl. cloudy, 1.5 hours; more cloudy than No. 1 in 5 hours at 0°
3	.0045	Li_2SO_4	.0500	Cloudy, 1.5 hours; more cloudy than No. 2 in 5 hours at 0°
4	.0082	Li_2SO_4	.0458	Sl. ppt., 1 hour; considerable ppt. in 2.5 hours at 0°
5	.0000	Rb_2SO_4	.0199	Cloudy, 5 hours at 0°
6	.0009	Rb_2SO_4	.0166	More cloudy than blank, No. 5, in 4.5 hours at 0°
7	.0018	Rb_2SO_4	.0166	Cloudy, 1.5 hours; ppt., 3.5 hours at 0°
8	.0031	Rb_2SO_4	.0142	Cloudy, 1 hour; ppt., 3 hours at 0°
9	.0066	Rb_2SO_4	.0166	Ppt., 0.5 hour at 0°
10	.0132	Rb_2SO_4	.0142	Cloudy, 0.5 hour at room temp.; sl. ppt., 1 hour, room temp.
11	.0000	Cs_2SO_4	.0127	Cloudy, 5 hours at 0°
12	.0005	Cs_2SO_4	.0116	No difference from blank No. 11, 5 hours at 0°
13	.0010	Cs_2SO_4	.0116	More cloudy than blank No. 5, 4.5 hours at 0°
14	.0045	Cs_2SO_4	.0116	Ppt., 1.5 hours at 0°
15	.0082	Cs_2SO_4	.0116	Opalescent, 1 hour at room temp., ppt., 0.5 hour at 0°
16	.0000	$MgSO_4$	.0550	Cloudy, 5 hours at 0°
17	.0005	$MgSO_4$	.0500	More cloudy than No. 16, 5 hours at 0°
18	.0010	$MgSO_4$	.0500	More cloudy than No. 16, 5 hours at 0°
19	.0045	$MgSO_4$	.0500	Cloudy and sl. ppt., 3.5 hours at 0°
20	.0082	$MgSO_4$	.0458	Cloudy, 1 hour; ppt., 2 hours at 0°

Discussion

The results indicate that zirconium sulfate will detect 1.0 mg. or more potassium in the presence of 50 mg. of lithium sulfate (Expts. 1–4), 16.6 mg. of rubidium sulfate (Expts. 6–10) or of 11.6 mg. of cesium sulfate (Expts. 11–15). It did not detect 0.5 mg. of potassium in the presence of 11.6 mg. of cesium sulfate (Expt. 12). It detected 0.5 mg. or more potassium in the presence of 50 mg. of magnesium sulfate (Expts. 16–20). To detect 1 mg. of potassium in the presence of any members of the fifth group, a comparison with a blank run should be made concurrently. With lithium or magnesium present, comparison with a blank should be made in testing for 4.5 mg. or less potassium (Expts. 3 and 19).

Comparison of Reagents for Potassium.—In order to compare zirconium sulfate, sodium cobaltic nitrite, chloroplatinic acid and perchloric acid as reagents for the fifth group elements, a series of tests was made as tests are usually made in qualitative analysis—adding the reagent to the solutions to be tested. None of the four reagents gave a precipitate with 11% sodium acetate, 5.5% magnesium sulfate or 5.5% lithium sulfate. Sodium cobaltic nitrite solution gave a slight precipitate with a saturated lithium sulfate solution. Sodium cobaltic nitrite and chloro-

platinic acid gave precipitates with 11% ammonium chloride, 1.92% rubidium sulfate and 1.16% cesium sulfate solutions as well as with 8.8% potassium sulfate solution. Perchloric acid gave a precipitate with the same solutions except the 1.16% cesium sulfate solution, but when a more concentrated cesium sulfate solution was prepared, it gave an immediate precipitate. *Zirconium sulfate gave a precipitate with the 8.8% potassium sulfate solution only.*

Reagents for the detection of potassium, other than zirconium sulfate, cannot be used in the presence of all members of the fifth group of metals. Sodium cobaltic nitrite, perchloric acid and chloroplatinic acid give a precipitate with rubidium and cesium as well as with potassium and ammonium. The perchloric acid method requires the use of absolute alcohol and the chloroplatinic acid requires the use of 80% alcohol to separate potassium from sodium and lithium.

Summary

Zirconium sulfate will detect 1.0 mg. or more of potassium in 2 cc. of reaction mixture in the presence of lithium, rubidium, cesium or magnesium ions, as well as those of sodium and ammonium. The detection of potassium by zirconium sulfate is accomplished without the use of alcohol or complicated procedure. It should always be used as the preliminary reagent, therefore, in looking for potassium, before going through the ordinary more complicated procedure.

COLUMBUS, OHIO

[Reprint from the Journal of the American Chemical Society, 51, 1311 (1929).]

[Contribution from the Chemical Engineering Department, The Ohio State University]

ZIRCONIUM. IV. PRECIPITATION OF ZIRCONIUM BY PHOSPHATES

By Rufus D. Reed and James R. Withrow

Received July 16, 1928 Published May 6, 1929

This paper is devoted to a study of the completeness of precipitation of zirconium by other phosphates. In testing for completeness of precipitation of potassium by zirconium sulfate it was found that this reagent also gave a precipitate with sodium cobaltic nitrite. Therefore, it became necessary to remove the zirconium before testing for potassium. As phosphates have been used for quantitatively determining zirconium and as Noyes and Bray[1] have shown that phosphates do not interfere with the detection of potassium by sodium cobaltic nitrite, the completeness of removal of zirconium by phosphates prior to testing for potassium was investigated.

The results indicated that a five-fold excess of ammonium phosphate, phosphoric acid or microcosmic salt in the presence of 0.344 molal sulfuric acid were all efficient in removing zirconium but that sodium phosphate was inefficient except when used in forty-fold excess. The presence of added acid was necessary.

Literature

Phosphates.—Sodium phosphate,[2] ammonium phosphate,[3] microcosmic salt[4] and phosphoric acid[5] have been used to determine zirconium quantitatively in the presence of sulfuric acid. Biltz and Mecklenburg[6] recommend the qualitative detection of zirconium by sodium phosphate in the presence of hydrochloric or nitric acid, as sulfuric acid slowed up the reaction.

Conditions for the Precipitation of Zirconium Phosphate.—Marden and Rich[2] recommend "a slight excess of sodium phosphate" in the presence of 10% sulfuric acid. Lundell and Knowles[3] recommend an excess of 10 to 100 times the calculated amount of ammonium phosphate in

[1] Noyes and Bray, This Journal, **31**, 634 (1909).
[2] Marden and Rich, *J. Ind. Eng. Chem.*, **12**, 654 (1920).
[3] Lundell and Knowles, This Journal, **41**, 1801 (1919).
[4] Steiger, *J. Washington Academy of Science*, **8**, 637 (1908).
[5] Marden and Rich, Bureau of Mines, Bulletin No. 186, 75–77 (1921).
[6] Biltz and Mecklenburg, *Z. angew. Chem.*, **25**, 2110 (1912).

the presence of 2 to 20% tepid sulfuric acid. Less than 0.5% sulfuric acid caused the formation of basic zirconium phosphate. Noyes, Bray and Spear[7] found that an excess of sodium phosphate was needed to remove practically all of the zirconium from solution. Steiger[4] stated that the zirconium was completely removed by microcosmic salt except when the acidity was from 5 to 10% sulfuric acid. Marden and Rich investigated the yield of zirconium phosphate by precipitation with various phosphates and concluded[5] "that $(NH_4)_2HPO_4$, Na_2HPO_4 or H_3PO_4 gave equally good results." If one chooses results from their determinations given in the table, agreeing results are secured, but the average of their determinations of zirconium by sodium phosphate is less than the average of either the ammonium phosphate or phosphoric acid results.

While zirconium has been determined quantitatively by all four phosphates, their efficiency in removing zirconium completely in the presence of hydrochloric, nitric and sulfuric acids of varying concentrations was still subject to question. It was decided, therefore, to investigate the completeness of removal of zirconium by these phosphates.

Experimental

Reagents.—The zirconium sulfate solution contained 0.1134 g. of zirconium sulfate per cc. The approximate strengths of the acids were determined by specific gravity. The phosphates were analyzed for phosphate by the magnesium pyrophosphate method according to Treadwell and Hall.[8]

General Procedure.—To 1-cc. portions of zirconium sulfate solution in the presence of no added acid and also hydrochloric, nitric or sulfuric acid, a solution of either phosphoric acid, sodium phosphate, microcosmic salt or ammonium phosphate was added. After standing for two hours or overnight the solutions were filtered through closest grained filter paper and washed four times with cold water. Early experiments showed that if medium texture paper was used the zirconium phosphate would pass through the paper. To make any precipitate more noticeable, the filtrate and washings were concentrated upon a sand-bath to 10 or 20 cc. Then concentrated ammonium hydroxide was added to neutralize the acid. If the solution gave no deposit, it was warmed and allowed to stand to see if a tardy precipitate would form.

Sodium phosphate as a reagent for precipitation of zirconium was investigated more minutely than the others as it would not interfere with the detection of potassium after zirconium was removed. The efficiency of all four reagents is shown in the table.

Discussion

In Expts. 1 to 4 where no acid was added the precipitate settled slowly and filtered with difficulty. In Expts. 5 to 25 where acid was added the precipitate settled readily and filtered much more rapidly than where no acid was added. Evidently acid must be added to secure a proper

[7] Noyes, Bray and Spear, THIS JOURNAL, **30**, 559–560 (1908).

[8] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, **1915**, Vol. II, p. 474.

TABLE I

PRECIPITATION OF ZIRCONIUM BY PHOSPHATES

Expt.	Added acid Kind	G.	Total vol., cc.	Ppt. calcd., P_2O_5	Calcd. factor as excess, P_2O_5	Test in filtrate for zirconium by NH_4OH Na_2HPO_4	H_3PO_4	$NaNH_4HPO_4$	$(NH_4)_2HPO_4$
1	None	....	50	0.5696	10.0	Ppt.	Ppt.	Ppt.	Sl. ppt.
2	None	....	200	2.2792	40	....	Clear No. ppt.	....	....
2a	None	....	50	2.2792	40.0	....	Few dark flocks	....	....
3	None	....	100	5.6980	100.0	....	Clear No ppt.	Sl. ppt.	....
4	None	....	200	1.1396	20.0	....	Dark ppt.	....	....
5	HCl	0.410	54	0.0929	1.33	Ppt.	....	....	....
6	HCl	.410	54	.0929	1.33	Ppt.	....	....	....
7	HCl	.373	50	.1139	2.00	Ppt.	....	....	....
8	HCl	9.325	50	.1139	2.00	Ppt.	....	....	....
9	HCl	0.373	50	.5696	10.00	Ppt.	Ppt.	Ppt.	Ppt.
10	HCl	1.230	152	2.0907	36.7	Sl. ppt. overnight	....	....	....
11	HCl	0.373	50	1.1396	20.0	....	Sl. ppt.	Sl. ppt.	Sl. if any ppt.
12	HCl	.373	50	2.8490	50.0	....	No ppt. clear	....	....
13	HNO_3	.358	50	0.2321	4.05	Sl. ppt. on standing	....	....	....
14	HNO_3	8.717	50	.2321	4.05	Ppt. on standing	....	....	....
15	HNO_3	4.3585	50	1.9658	32.4	Ppt. on standing	....	....	....
16	HNO_3	0.896	50	0.5696	10.0	Ppt. on standing	Sl. ppt.	Ppt.	Sl. ppt.
17	HNO_3	.8966	50	1.1396	20.0	....	Clear No ppt.	Clear No ppt.	Sl. if any ppt.
18	H_2SO_4	.1634	50	0.5405	9.48	....	....	....	Ppt. standing
19	H_2SO_4	.817	50	.2849	5.00	....	Cloudy	Ppt.	Clear No ppt.
20[a]	H_2SO_4	.817	50	.5696 / .5405	10.0	Ppt. on standing	Sl. ppt.	Clear No ppt.	Clear No ppt.
21	H_2SO_4	1.634	50	.2849	5.0	....	Clear No ppt.	Clear No ppt.	Slight if any ppt.
22	H_2SO_4	1.6417	50	.4642	8.15	Ppt. on standing	....	....	....
23	H_2SO_4	1.634	50	.5698	10.0	....	Clear No ppt.	Clear No ppt.	Clear No ppt.
24	H_2SO_4	3.2324	100	.3215	40.05	No ppt.	....	....	....
25	H_2SO_4	8.17	50	.5718	10.0	....	....	Sl. cldy.	Clear No ppt.

[a] The amount of ammonium phosphate used in Expt. 20 was not 0.5696 g. of P_2O_5 as in the other three cases but 0.5405 g. of P_2O_5. All other conditions were the same.

physical condition of the precipitate. In Expts. 18 to 25, where sulfuric acid was present, the precipitate formed only after standing for a few seconds, while in all other cases, Expts. 1 to 17, where either none or hydrochloric or nitric acid was present, it formed as soon as any precipitant was added. This agreed with the observation of Biltz and Mecklenburg.[6]

In Expt. 5 the zirconium was precipitated from hot solution while in Expt. 6 the precipitation was made from solution at room temperature,

all other conditions being equal. The bulk of precipitate was greater in the filtrate from 5 than from 6, possibly indicating that zirconium was more completely removed when precipitation was made at room temperature than from hot solution. All other precipitations were made at room temperature.

Effect of Added Acid.—In Expts. 5 to 12 where hydrochloric acid was present, only one condition—Expt. 12, 0.204 *N* hydrochloric acid—succeeded in removing all of the zirconium. An excess of 50 times the calculated amount of phosphoric acid was needed for this. Expts. 13–17, where 0.269 *N* nitric acid was present, indicated that in Expt. 17, 20 times the calculated needed amount of phosphoric acid, microcosmic salt or ammonium phosphate would remove all of the zirconium from solution. Expts. 18 25, in which sulfuric acid was present, indicated that either phosphoric acid, microcosmic salt or ammonium phosphate—Expts. 20, 21, 23—when used in excess of 5 to 10 times the calculated needed amount would remove all of the zirconium from solution in the presence of 0.817 g. (0.168 molal or 0.334 normal) to 1.634 g. (0.334 molal or 0.668 normal) of sulfuric acid per 50 cc. of solution. Expt. 25 showed that as much as 8.17 g. of sulfuric acid per 50 cc. of solution did not prevent the complete removal of zirconium by 10 times the calculated amount of ammonium phosphate. These results indicated that the presence of sulfuric acid, while retarding the appearance of a precipitate, was more beneficial than either hydrochloric or nitric acid in aiding the removal of zirconium by phosphates.

Efficiency of Various Phosphates.—Sodium phosphate—Expts. 19 to 23—was less efficient than phosphoric acid, microcosmic salt or ammonium phosphate in removing zirconium from solution. However, the amount of zirconium left in solution by sodium phosphate was very small and the precipitate of zirconium phosphate formed only after standing. The bulk of the deposits, in the ammonium phosphate column, marked "slight if any" amounted to but a few flakes which would be unweighable on ignition and might have been shreds of filter paper.

Summary

1. The efficiency of sodium phosphate, phosphoric acid, ammonium phosphate and microcosmic salt as precipitants for zirconium has been investigated and the last three were found to be equally efficient and more efficient than sodium phosphate. Even sodium phosphate removed practically all of the zirconium.

2. The phosphates were found most efficient in the presence of 0.344 to 0.668 *N* sulfuric acid and less efficient in the presence of 0.269 *N* nitric acid or 0.204 *N* hydrochloric acid.

3. Although record was found in the literature of the formation of

basic zirconium phosphate in the absence of added acid, no record was found indicating incompleteness of precipitation of zirconium under these conditions. Investigation showed that phosphates are not efficient in removing zirconium in the absence of added acid.

COLUMBUS, OHIO

[Reprint from the Journal of the American Chemical Society, **51**, 3238 (1929).]

[Contribution from the Chemical Engineering Department, The Ohio State University]

ZIRCONIUM. V. DETECTION OF TRACES OF POTASSIUM IN THE PRESENCE OF ZIRCONIUM[1]

By Rufus D. Reed and James R. Withrow

Received May 23, 1929 Published November 8, 1929

Zirconium sulfate can be used to detect potassium,[2] but the completeness of precipitation of potassium by zirconium sulfate is not easily measured, as zirconium sulfate also gives a precipitate with sodium cobaltic nitrite. Obviously zirconium must be eliminated, if present, prior to testing for potassium, so a study of delicate methods of detection of traces of potassium under these conditions was made. The results indicated that while phosphates will remove the zirconium, they interfere with the subsequent detection of traces of potassium. Ammonium hydroxide, however, was found to remove all of the zirconium without interfering materially with subsequent detection of potassium. Also a quicker and less objectionable method was found to be the transformation of the zirconium into a complex ion with tartaric acid, and after adjusting the acidity with sodium hydroxide and acetic acid, testing for potassium with sodium cobaltic nitrite.

Discussion of Literature

Zirconium can be removed by phosphates in excess under proper conditions.[3] Bray[4] found that dilute sodium phosphate solution gave no precipitate with sodium cobaltic nitrite; but according to solubility records[5] approximately 39 cc. of water at 20° would be needed to dissolve the 7.5 g. of sodium phosphate which we found was needed to remove 0.1134 g. of zirconium sulfate used in the test. If the original concentration of potassium was 1 mg. per cc., this dilution would lower the concentration to 0.02 mg. per cc.—a smaller concentration than sodium cobaltic nitrite will detect.[2]

Smaller concentrations of phosphoric acid, microcosmic salt or ammonium phosphate would remove the zirconium but the interfering ammonium salts would have to be expelled before testing for potassium. The gelatinous zirconium phosphate might adsorb any traces of potassium salts. The use of ammonium hydroxide to remove the zirconium risked the same objections.

[1] Presented at the Columbus Meeting of the American Chemical Society, April 25, 1929.

[2] Reed and Withrow, This Journal, **50**, 1515 (1928).

[3] Reed and Withrow, *ibid.*, **51**, 1311 (1929).

[4] Bray, *ibid.*, **31**, 634 (1909).

[5] Seidell, "Solubility of Inorganic and Organic Compounds," D. Van Nostrand Co., New York, 2d ed., **1919**, p. 662.

The possibility of avoiding these dangers of loss of potassium by volatilization or adsorption, by the elimination of zirconium as a complex ion was suggested by the statement of Fresenius,[6] "tartaric acid prevents the precipitation (of zirconium) by alkalies."

Experimental

Detection of Potassium after Removal of Zirconium.—Samples containing 0.113 g. of zirconium sulfate, varying amounts of potassium and 1.634 g. of hydrogen sulfate were prepared. Some were treated with an excess of 5 times the calculated needed amount of either phosphoric acid, ammonium phosphate or microcosmic salt. To avoid evaporation of large amounts of solution the final volume was kept at 50 cc. After standing for several hours the solutions were filtered and the filter washed four times with cold water. The filtrate and washings were evaporated to a sirup. This was transferred with washing to a platinum crucible, the evaporation continued to dryness and the residue ignited short of red heat until no more fumes were noticed. If a drop of a solution prepared by adding 1 cc. of water to the residue gave no test for ammonium salts with Nessler's reagent, the remainder was neutralized with sodium hydroxide, about 3 cc. of 30% acetic acid was added and then an equal volume of sodium cobaltic nitrite solution. Preliminary experimentation showed that if this excess acid was not added a flaky precipitate was obtained whether potassium was present or not. This amount of acetic acid did not prevent the detection of 0.3 mg. of potassium in a test solution. Other samples were treated with ammonium hydroxide instead of phosphates to remove the zirconium and the filtrates were tested for potassium in the same way except that no acetic acid was added. The results appear in Table I.

Table I

Detection of Potassium by Sodium Cobaltic Nitrite after Removal of Zirconium

Expt.	K, g. per sample	Results of test for potassium by $Na_3Co(NO_2)_6$ after removing zirconium by H_3PO_4	$NaNH_4HPO_4$	$(NH_4)_2HPO_4$	NH_4OH
1	0.00053	Flaky ppt.	Flaky ppt.	Clear, sev. hrs.	Ppt., 4 min.
2	.00031	Clear, 20 min.; cloudy, 2 hrs.	Ppt., 45 min.	Clear, no ppt., sev. hrs.	Ppt., 5 min.
3	.00012	Clear, no ppt., 1 hr.	Clear, no ppt., 1 hr.	Clear, no ppt., sev. hrs.	Sl. ppt., standing hrs.
4	.00000	Clear, no ppt., 15 min.; cloudy, 1 hr.	Clear, 1 hr.	Clear, 20 min.; cloudy, 40 hrs.	Clear, no ppt., 1 day
5	.00176	.....	.....	Ppt. at once	

Discussion.—The precipitates (Run 1) where zirconium had been removed by phosphoric acid or microcosmic salt were flaky and brownish, not the usual yellow color of potassium cobaltic nitrite. They resembled the precipitates obtained (preliminary work) by adding sodium cobaltic nitrite to a solution of phosphoric acid neutralized by sodium hydroxide which had added thereto but a small excess of acetic acid.

The results in Cols. 2, 3 and 4, where zirconium was removed by phosphates prior to testing for potassium, indicated that either the zirconium phosphate adsorbed the potassium or the prolonged heating, needed to

[6] Fresenius, "Qualitative Chemical Analysis," translated by C. A. Mitchell, John Wiley and Sons, Inc., New York, 1921, 17th German ed., p. 181.

drive off the excess acids and ammonium salts, volatilized most or all of the potassium. When zirconium was removed by ammonium hydroxide (Col. 5), prior to testing for potassium, there were no such difficulties in detecting potassium. Therefore phosphates are not suitable and *ammonium hydroxide is suitable for removing zirconium prior to testing for potassium by sodium cobaltic nitrite.*

Detection of Potassium in the Presence of Zirconium by Changing the Zirconium into a Non-Interfering Complex Ion with Tartaric Acid.—Preliminary experimentation showed that if a 2-cc. solution of zirconium sulfate be treated with 0.3 g. of tartaric acid and the acidity controlled by neutralizing with 25% sodium hydroxide, making slightly acid with acetic acid, no precipitate is obtained with sodium cobaltic nitrite. If any potassium was added, a test for it was obtained. To determine the sensitiveness of sodium cobaltic nitrite for potassium under these conditions, a series of experiments was run. The manipulation was exactly as described above. The amount of zirconium sulfate was 0.1131 g. per test, the tartaric acid 0.3 g. and the amount of potassium varied. The results appear in Table II.

TABLE II

SENSITIVENESS OF SODIUM COBALTIC NITRITE FOR POTASSIUM WHEN ZIRCONIUM IS PRESENT IN COMPLEX ION

Expt.	K, g. per sample	Results of test for potassium with $Na_3Co(NO_2)_6$: Presence of zirconium	Absence of zirconium K_2SO_4 alone present
1	0.00107	Cloudy at once; ppt., 5 min.	Ppt., 5 min.
2	.00072	Cloudy, 5 min.	Sl. ppt., 5 min.
3	.00053	Cloudy, 10 min.	Very sl. ppt., 10 min.
4	.00030	Very sl. cloudy, 15 min.; ppt., 1.5 hrs.	Very sl. ppt., 10 min.
5	.00014	Very sl. cloudy, 1.5 hrs.; no ppt., 2 hrs.	Ppt., 2.5 hrs.
6	.00000	No ppt.; clear, 1.5 hrs.	Clear, no ppt., 23 hrs.

Discussion.—The suppression of zirconium by tartaric acid did not prevent the detection of 0.3 mg. of potassium (Expt. 4) by sodium cobaltic nitrite. The slight difference between the time for appearance of a precipitate in the test for potassium in the presence (Expt. 4) and absence of zirconium was doubtless due to dilution of potassium solution from 1 cc. to 3 cc. with zirconium present.

This method of suppression of zirconium ions is much to be preferred to removal of zirconium by either phosphates or ammonium hydroxide prior to testing for potassium by sodium cobaltic nitrite, as it is shorter and avoids danger of adsorption or volatilization of potassium.

Summary

1. The use of phosphates to remove zirconium prior to testing for potassium by sodium cobaltic nitrite is not advisable because of loss or dilution of potassium.

2. When phosphoric acid is neutralized with sodium hydroxide and the solution tested with sodium cobaltic nitrite, a misleading precipitate is secured unless a considerable excess of acetic acid is added.

3. Zirconium can be removed by ammonium hydroxide and potassium detected in the filtrate by sodium cobaltic nitrite, after eliminating the ammonium.

4. The best and shortest way of eliminating zirconium prior to testing for potassium by sodium cobaltic nitrite is by throwing the zirconium into a complex ion with tartaric acid and controlling the acidity with sodium hydroxide and acetic acid.

COLUMBUS, OHIO

AUTOBIOGRAPHY

I, Rufus Daniel Reed, was born near Blanchester, Ohio, September 12, 1894. I received all my primary and secondary school education in the public schools of the village of Blanchester, Ohio; my undergraduate education, at Wilmington College, from which I obtained the Degree of Bachelor of Science in 1919. I received the Degree of Master of Arts from the Ohio State University in 1920. While in residence at the Ohio State University I acted in the capacity of Graduate Assistant in Chemistry during the year of 1919 and 1920. In 1928 I received from the Ohio State University the Degree of Doctor of Philosophy.